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Spectroscopic investigation and vibrational analysis of paraldehyde by FTIR and laser Raman techniques

S Gunasekaran* and Leela Abraham[1]
PG Department of Physics, Pachaiyappa's College, Chennai-600 030, India
[1]Department of Physics, The Ethiraj College for Women, Chennai-600 008, India
E-mail : guna_pachai@hotmail.com

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Abstract : Paraldehyde is a trimer of acetaldehyde formed from this under acid catalysis. It falls under the broad classification of the sedative hypnotics used as anti-convulsant in eplepticus and tetanus. The work presents vibrational band analysis on the molecular structure of the compound paraldehyde through infrared and Raman spectral measurements. Normal coordinate analysis has been carried out with a new set of symmetry coordinates to obtain the molecular force field of the system based on C_{3v} point group symmetry. Potential energy distribution evaluated for all the normal modes of vibration, confirm that the chosen set of vibrational frequencies contribute maximum to the potential energy associated with the normal coordinates of the molecule.

Keywords : Vibrational spectroscopy, paraldehyde, normal coordinate analysis, potential energy distribution.

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1. Introduction

Paraldehyde is a hypnotic drug belonging to the aldehyde group under the sedative hypnotic classification. Among aldehydes, acetaldehyde is the most common and is used as a trimer *i.e.* paraldehyde. The presence of lone pair on electrons on the oxygen atom of the carbonyl group imparts to aldehydes several characteristic features which are not found in other compounds. Though spectral investigation on aldehydes has been carried out by many, not much work is done on paraldehyde as such [1–5]. The present work is to make use of infrared and Raman spectroscopic methods in the structural elucidation of paraldehyde. A new set of symmetry coordinates have been constructed on the basis of C_{3v} symmetry and a normal coordinate analysis has been carried out.

2. Experimental details

The Fourier transform infrared (FTIR) spectrum of the sample paraldehyde is reported in the region 4000–400 cm^{-1}. The spectrum was recorded on a BRUKER IFS 66V spectrophotometer with a resolution of 0.5 cm^{-1}. All the sharp bands of the spectrum have an accuracy of ±1 cm^{-1}. The sample in the form of liquid is housed in a purgeable chamber whose windows are composed of KBr. The laser Raman spectrum of the same sample was recorded on a DILOR Z 24 spectrophotometer using argon ion laser source. The monochromator consists of 3 holographic gratings having 1800 lines to a millimeter. The spectra are presented in Figures 1 and 2.

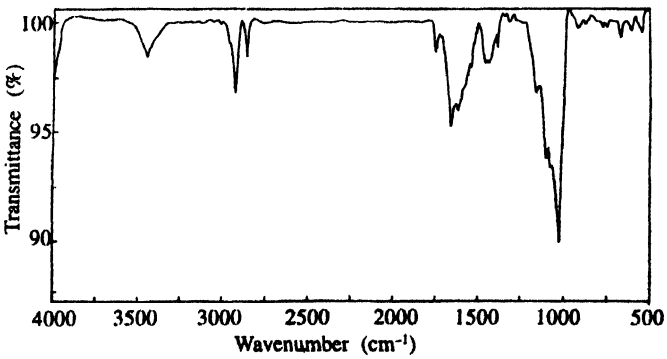

Figure 1. FTIR spectrum of paraldehyde (4000–500 cm^{-1}).

*Corresponding Author

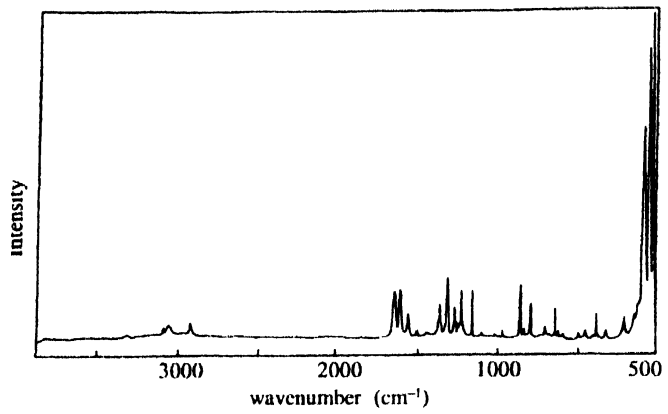

Figure 2. Laser Raman spectrum of paraldehyde (3500–250 cm $^{-1}$)

3. Vibrational analysis

Paraldehyde has 30 modes of vibration and are distributed as $\Gamma_{vib} = 7A_1 + 3A_2 + 10E$. A_1 and E are both infrared and Raman active while A_2 mode is inactive under the C_{3v} point group selection rules. The assignment to various fundamental modes are in agreement with the literature values.

The structure, orientation of the principal axes and the nomenclature of the parameters of the paraldehyde molecule is shown in Figure 3. Changes in the interaction distances, the interbond angles and the angular parameters associated with the in-plane vibrations, have been considered for the internal coordinates of the molecule.

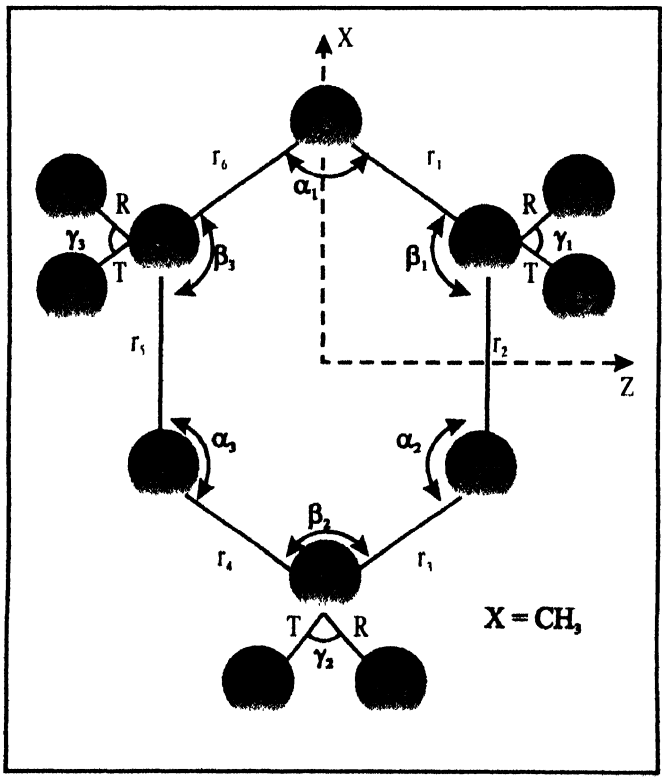

Figure 3. The structure and the nomenclature of the parameters of the paraldehyde molecule.

Symmetry coordinates have been arrived at with the knowledge of projection operators and the character table pertaining to the C_{3v} point group symmetry. The symmetry coordianates thus obtained, are as follows.

A_1 species :

$$s_1 = 1/6^{1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6),$$

$$s_2 = 1/3(\Delta R_1 + \Delta R_2 + \Delta R_3),$$

$$s_3 = 1/6^{1/2}(\Delta R_1 + 2\Delta R_2 + \Delta R_3),$$

$$s_4 = 1/3^{1/2}(\Delta T_1 + \Delta T_2 + \Delta T_3),$$

$$s_5 = 1/6^{1/2}(\Delta T_1 - 2\Delta T_2 + \Delta T_3),$$

$$s_6 = 1/6^{1/2}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3),$$

$$s_7 = 1/3^{1/2}(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3).$$

E species :

$$s_{8a} = 1/12^{1/2}(-2\Delta r_1 + \Delta r_2 + \Delta r_3 - 2\Delta r_4 + \Delta r_5 + \Delta r_6),$$

$$s_{8b} = 1/2(\Delta r_2 - \Delta r_3 + \Delta r_5 - \Delta r_6),$$

$$s_{9a} = 1/12^{1/2}(-\Delta r_1 + 2\Delta r_2 - \Delta r_3 - \Delta r_4 + 2\Delta r_5 - \Delta r_6),$$

$$s_{9b} = 1/2(\Delta r_1 - \Delta r_3 - \Delta r_4 - \Delta r_6),$$

$$s_{10a} = 1/12^{1/2}(-2\Delta r_1 - \Delta r_2 + \Delta r_3 + 2\Delta r_4 + \Delta r_5 - \Delta r_6),$$

$$s_{10b} = 1/2(\Delta r_2 + \Delta r_3 - \Delta r_5 - \Delta r_6),$$

$$s_{11a} = 1/12^{1/2}(\Delta r_1 + 2\Delta r_2 + \Delta r_3 - \Delta r_4 - \Delta r_5 - \Delta r_6),$$

$$s_{11b} = 1/2(-\Delta r_1 + \Delta r_3 + \Delta r_4 - \Delta r_6),$$

$$s_{12a} = 1/6^{1/2}(\Delta R_1 + 2\Delta R_2 - 2\Delta R_3),$$

$$s_{12b} = 1/2^{1/2}(\Delta R_1 - \Delta R_2),$$

$$s_{13a} = 1/6^{1/2}(\Delta T_1 - \Delta T_2 - \Delta T_3),$$

$$s_{13b} = 1/2^{1/2}(-\Delta T_2 + \Delta T_3),$$

$$s_{14a} = 1/12^{1/2}(-\Delta\alpha_1 + 2\Delta\alpha_2 + \Delta\alpha_3 - \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3),$$

$$s_{14b} = 1/2(\Delta\alpha_2 - \Delta\alpha_3 + \Delta\beta_2 - \Delta\beta_3),$$

$$s_{15a} = 1/12^{1/2}(-2\Delta\alpha_1 - 2\Delta\alpha_2 + \Delta\alpha_3 + 2\Delta\beta_1 + \Delta\beta_2 - \Delta\beta_3),$$

$S_{15b} = 1/2(\Delta\alpha_2 + \Delta\alpha_3 - \Delta\beta_2 - \Delta\beta_3)$,

$S_{16a} = 1/6^{1/2}(\Delta\gamma_1 - 2\Delta\gamma_2 + \Delta\gamma_3)$,

$S_{16b} = 1/2^{1/2}(-\Delta\gamma_1 + \Delta\gamma_3)$,

$S_{17a} = 1/6^{1/2}(-2\Delta\gamma_1 - \Delta\gamma_2 - \Delta\gamma_3)$,

$S_{17b} = 1/2^{1/2}(-\Delta\gamma_2 - \Delta\gamma_3)$.

From the data available in literature, it is found that the intensities of the carbonyl bands of aldehydes vary with structural features. In alcoholic solution, there is a distinct fall in the intensity of aldehyde carbonyl absorptions. Ashdown and Kletz [6] have reported the number of such cases and the range of frequencies 1020–1110 cm^{-1} to be associated with the C–O linkage. In the present case, the frequencies 1022, 1095, 1155, 1275 and 1317 cm^{-1} are assigned to C–O stretching vibrations, while the same are identified at 1035, 1130, 1189 and 1200 cm^{-1} in the Raman spectrum. C–H stretching vibrations are highly characteristic and aldehydes show absorption in this region from the valence vibration of the hydrogen atom attached to the carbonyl group. This is found in the region 2900–2700 cm^{-1} [7]. Many aldehydes exhibit two bands in this region one at 2720 cm^{-1} and the other at 2820 cm^{-1}, the doubling being due to a Fermi resonance between υ_{CH} and the first overtone of the C–H deformation [8,9]. In the present work, the bands at 2851, 2921 and 3000 cm^{-1} are assigned to C-H stretching vibrations. The bending modes normally mainfest at much lower frequencies than the stretching mode. In the IR spectra of paraldehyde, bending modes of CCH deformations are observed at 1317 and 1340 and 1375 cm^{-1}. Bands of very weak intensity observed at 543, 599 and 669 cm^{-1} have been identified as due to C–O–C/O–C–O bending vibrations [10]. In the Raman spectrum, these vibrations are found at 550 cm^{-1} and at 655 cm^{-1} as a strong and weak band respectively. C–CH_3 vibrations have been identified in the broad region 949–1164 cm^{-1}. Accordingly bands at 1075, 1095 and 1240 cm^{-1} are assigned to C–CH_3 vibrations.

The method of kinetic constants has been used to solve the secular equation [11–13]. Frequency assignment has been verified by evaluating the potential energy distribution (PED) using the relation PED = $F_{ik}L_{ik}^2/\lambda_k$, where PED is the contribution of the i-th symmetry coordinate to the potential energy of vibration whose frequency is ν_k, F_{ik} is the force constant, L_{ik} is the L matrix element and $\lambda_k = 4\pi^2C^2\nu_k^2$.

4. Conclusion

A detailed vibrational band assignment has been carried out for the paraldehyde molecule. The PED evaluated serves as a check as to whether tha normal modes of vibration contribute maximum to the potential energy distribution. The initial set of force constants have been taken from literature on related compounds [14,15]. The final set of constants has been arrived at by a refinement process.

The vibrational band assignments together with the PED calculated are presented in Table 1. The initial and final set of force constants are presented in Table 2. The frequency assignment for C–O stretching vibrations in the range of 1020–1317 cm^{-1} is justified by the significant contribution of this mode to the potential energy distribution with the force constant of this mode agreeing with the literature values. The symmetric and asymmetric C–CH_3 vibrations assigned to the bands at 1075, 1095 and 1240 cm^{-1} in the infrared spectra, correspond to force constant with a contribution of over

Table 1. Fourier transform infrared and laser Raman frequencies and potential energy distribution of paraldehyde.

Frequency (cm^{-1})		Description	PED%
IR	Raman		
1022 (vs)	1025	υ_1 C–O symmetric stretching	98
1075 (vs)	1050	υ_2 C–CH_3 symmetric stretching	99
1095 (m)	1118	υ_3 C–CH_3 asymmetric stretching	95
2851 (vw)	2859 (w)	υ_4 C-H symmetric stretching	38
2921 (w)	2946 (w)	υ_5 C–H asymmetric stretching	37
543 (vw)	550 (s)	υ_6 C–O–C/O–C–O bending	62
1317 (vw)		υ_7 CCH bending	35
1095 (m)	1130	υ_8 C–O asymmetric stretching	48
1155 (w)	1189	υ_9 C–O asymmetric stretching	84
1275 (vw)	1200	υ_{10} C–O asymmetric stretching	70
1317 (vw)		υ_{11} C–O asymmetric stretching	82
1240 (vw)		υ_{12} C–CH_3 asymmetric stretching	96
3000 (vw)		υ_{13} C–H asymmetric stretching	32
599 (vw)		υ_{14} C–O–C/O–C–O bending	54
669 (vw)	655	υ_{15} C–O–C/O–C–O bending	65
1340 (vw)		υ_{16} CCH bending	43
1375 (vw)	1379 (w)	υ_{17} CCH bending	38

vs–very strong s–strong m–medium w–weak vw–very weak

to the PED of these mode. C–O–C/O–C–O bending vibrations contribute moderately to the PED of this mode with the force contant of this mode being in the range of 0.7–0.8 N/M. Thus, a normal coordinate analysis has been carried out successfully on the paraldehyde molecule with C_{3v} point group symmetry.

Table 2. Inital and final set of force constant values for paraldehyde (10^2 N/m).

Symmetry coordiantes	Parameter	Initial	Final
S_1	F_{11}	5.0523	5.0489
S_2	F_{22}	4.7259	4.7286
S_3	F_{33}	4.8635	4.8659
S_4	F_{44}	5.5316	5.5382
S_5	F_{55}	5.8103	5.815
S_6	F_{66}	0.7432	0.7456
S_7	F_{77}	1.0123	1.0169
S_8	F_{88}	5.5321	5.5362
S_9	F_{99}	5.6925	5.6946
S_{10}	$F_{10\,10}$	5.5526	5.5546
S_{11}	$F_{11\,11}$	5.6072	5.6049
S_{12}	$F_{12\,12}$	4.7325	4.7356
S_{13}	$F_{13\,13}$	5.2791	5.2813
S_{14}	$F_{14\,14}$	0.7989	0.8136
S_{15}	$F_{15\,15}$	0.7526	0.7583
S_{16}	$F_{16\,16}$	1.1301	1.1325
S_{17}	$F_{17\,17}$	1.0893	1.1135

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